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DESIGN AND CHEMICAL SYNTHESIS OF IODINE-CONTAINING MOLECULES
FOR APPLICATION TO SOLAR-PUMPED I* LASERS

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(NASA-CR-180297) DESIGN AND CHEMICAL
SYNTHESIS OF IODINE-CONTAINING MOLECULES FOR
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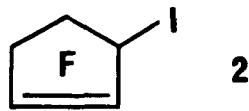
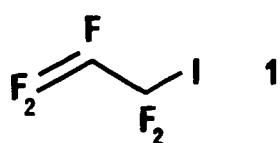
Our research is directed toward the design and synthesis of new media for solar-pumped I* lasers. In our original proposal to NASA, we outlined a wide-ranging study of diverse structures, containing iodine bound to various other atoms. Since the most effective existing lasants are perfluoroalkyl iodides, we have proposed a strategy for the development of improved materials of this type with absorption maxima at 300 nm. We also envisioned the synthesis and evaluation of other prototypical lasants containing iodine bound to boron, germanium, and several transition metal atoms.

Most of our work described in previous reports has been concerned with the fluorocarbon iodides, and some additional developments in that area are presented herein, together with an assessment of the prospects for further improvement. Additional informative results obtained during the current six-month period involve molecules containing iodine bound to atoms other than carbon. Previously our efforts to prepare such species were unsuccessful, except in the case of a germanium compound, $(CF_3)_3GeI$. We have now synthesized and measured absorption spectra for prototypical species containing iodine bound to boron, iron, and cobalt. Thus, some important data are now available for nearly all classes of prospective lasants outlined in our original proposal.

Fluorocarbon Iodides

In previous proposals and reports we have analyzed the structures and absorption spectra of various iodo fluorocarbons, in an effort to identify features which could shift the absorption maxima of these species to longer wavelength. This analysis led to our study of perfluoroallylic iodides, which would furnish especially stable perfluoroallylic radicals upon photodissociation. We prepared the prototypical molecules 1 and 2, and found that their

absorptions were not shifted significantly. As indicated in our last report,



the completion of these studies for publication was unexpectedly complicated by difficulties in the preparation of 2. Since we have already established that this approach will probably not yield a satisfactory lasant, we subsequently decided to forego further studies of 1 and 2, and to concentrate on investigation of new types of prospective lasants instead.

Since our last report, we have obtained uv spectra for two additional types of fluorocarbon iodides. Both of these species are available commercially. All of the spectra described herein were obtained in dilute methylene chloride (CH_2Cl_2) solution; the positions of the absorptions in the vapor phase should not differ significantly.

We first examined iodotrifluoroethylene, $\text{F}_2\text{C}=\text{CFI}$. To our knowledge, the absorption spectrum for a perfluorovinylic iodide had not been described previously. Since the carbon-iodine bond in such a compound is unusually strong, our previous correlation of absorption maxima with structure suggested that these species should absorb at relatively short wavelengths. However, the earlier analysis indicated incorrectly that the allylic compounds should absorb at long wavelength, and investigation of the readily available vinylic compound therefore seemed warranted. In solution the first absorption maximum of $\text{F}_2\text{C}=\text{CFI}$ was at 272 nm.

We also studied the diiodide, 1,2-diiodotetrafluoroethane ($\text{ICF}_2\text{CF}_2\text{I}$). Some dihalides are good quenchers of excited halogen atoms. However, our collaborator, Professor Stephen R. Leone, has previously observed enhanced

absorption intensity in $\text{BrCF}_2\text{CF}_2\text{I}$, relative to either $\text{C}_2\text{F}_5\text{Br}$ or $\text{C}_2\text{F}_5\text{I}$.¹ Since an increase in intensity can compensate to some extent for an absorption maximum at shorter wavelength than desired, we have looked at the prototypical diiodide. In solution, the absorption maximum was at 278 nm. The extinction coefficient of 128 was not increased significantly relative to simple monoiodo compounds, and the position of the absorption likewise was not shifted significantly.

A wide range of fluorocarbon iodides have now been evaluated as prospective lasants. The most promising compound by far appears to be perfluoro-tert-butyl iodide, $(\text{CF}_3)_3\text{CI}$. Unfortunately, the structural features responsible for its absorption maximum at 290 nm have not yet been clearly delineated. Although further shift to the red via modification of this structure is certainly plausible, we can presently discern no clearcut rational strategy for the design of more effective analogues. The synthesis of the desired materials could also be problematic, as in the case of $(\text{CF}_3)_3\text{CI}$ itself.

Boron Iodides

As reported earlier, preliminary studies in the Leone group showed that BI_3 absorbs strongly at wavelengths greater than 300 nm and affords I^* upon photodissociation.² Although this simple molecule was not expected to be a satisfactory lasant, these results do suggest that closely related species, $(\text{CF}_3)_2\text{BI}$ or BF_2I , might be effective.

Preparations of a few trifluoromethyl-substituted boron compounds have been reported.³ Although these species are clearly susceptible to decomposition via loss of difluorocarbene ($\text{F}_2\text{C}:)$, they have been isolated and characterized in a few cases. In contrast with the unknown perfluoroalkyl-

boron iodides, the analogous dialkylboron iodides (e.g., $(CH_3)_2BI$) are well known. Since the positions of the absorption maxima in iodo alkanes and the analogous perfluoroalkyl iodides generally do not differ markedly, we believe that the dialkylboron iodides should be appropriate model compounds for the desired fluoroalkyl species. Accordingly we have undertaken the synthesis of $(CH_3)_2BI$, to ascertain the positions of its absorptions and carry out preliminary photodissociation studies if appropriate. The desired material has reportedly been prepared as follows:⁴



In our hands, this procedure has initially furnished the related compound CH_3Bi_2 . In solution, this species has no absorption above 250 nm. The compound apparently decomposes in solution, as indicated by formation of material (probably I_2) absorbing at 520 nm.

This result suggests that $(CH_3)_2Bi$ probably will also lack an absorption at the requisite wavelength. Nonetheless, we will pursue our efforts to prepare this material by modifying the synthetic protocol. The results of these experiments will be reported in due course by Prof. Leone.

The synthesis of BF_2I remains a worthwhile objective, but we have been unable to pursue this possibility.

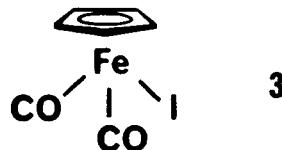
Transition Metal Iodides

A final major goal of our study has been the preparation and evaluation of various transition metal iodides. A major concern *a priori* was ensuring adequate volatility for these species. We anticipated that perfluoroalkyl ligands would be advantageous in this regard, and that these groups could

also confer other desirable characteristics, as in the perfluoroalkyl iodides. Our early efforts to prepare transition metal iodides bearing perfluoroalkyl substituents were thwarted by the finding that many such species (e.g., $(CF_3)_3TiI$) decompose readily via expulsion of difluorocarbene ($F_2C:$). However, we have subsequently found that species of this type containing other metals are known to be thermally stable. Other small ligands such as carbonyl (coordinated carbon monoxide, CO) should also enhance volatility.

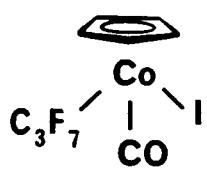
A second crucial consideration is the possible cleavage of these other ligands, rather than iodide, in photodissociation. Indeed, some published work substantiates the propensity of transition metal halides to lose other ligands upon photolysis,⁵ although the behavior of the particular compounds of interest to us remained to be explored.

To this end, we first examined cyclopentadienyliron dicarbonyl iodide (3), since this compound is commercially available. Its absorption spectrum

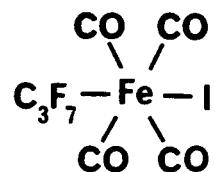


in solution was promising, but efforts in the Leone group to obtain a vapor-phase spectrum, via sublimation of the solid, resulted in decomposition.

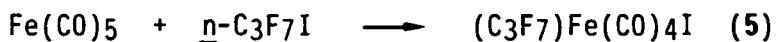
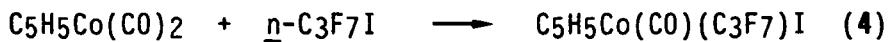
We then prepared the cobalt iodide 4 and a second iron compound, 5, via published procedures:^{6,7}



4



5



We anticipated that these species would be sufficiently volatile to permit some vapor-phase studies, since both were sublimed in the final stages of the literature preparations. In solution, both compounds have strong long-wavelength absorptions: for 4, 408 nm (extinction coefficient 3690), 288 (15,500), and 257 (26,400); for 5, 418 (527), 314 (4,449), and 261 (20,718). The 314 nm band of 5 appears especially intriguing. Prof. Leone will report the results of photodissociation studies which have recently been initiated in his laboratory. Useful variation and control of the photofragmentation behavior of these families of compounds may be attainable via alteration of the non-halogen ligands.

Other, fundamentally different types of transition metal iodides (e.g., TiF_3I) remain worthy objectives for future study.

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